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Water-Soluble and Optically pH-Sensitive Single-Walled Carbon Nanotubes from Surface Modification

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Received July 25, 2002

There is great interest in using single-walled carbon nanotubes (SWNTs) as nanoscale probes and sensors in biological electronics and optical devices because the electronic and optical properties of SWNTs are extremely sensitive to the surrounding environments.[1−5] For the applications of SWNTs-based sensors in a biological environment, an immediate question is how the sensors respond to the biological conditions such as pH,[5c] glucose, various ions, and proteins. This study requires a well-controlled modification of SWNT surfaces to obtain interfaces that are sensitive to these variables.[6] The exploration in this exciting area is still not in full blossom, partially due to the difficulty in preparing water-soluble SWNTs while maintaining the SWNT electronic structure intact.[4] In light of recent great progress in solubilization of SWNTs in various solvents by polymer wrapping and sidewall functionalization,[3a,4,5b,7−10] a better controlled modification of SWNT surfaces may be realized soon. In this work, we report a facile chemical routine to prepare water-soluble SWNTs that still retain their van Hove singularities after oxidative treatment.[7] The solubility in water for as-treated SWNTs with modified surfaces provides us with a unique opportunity to reveal the relationship of their electronic and optical properties with pH. Here we observe that after surface modification with carboxylate groups, the optical absorption of as-prepared water-soluble semiconducting SWNTs (Tube@Rice and HiPco) reversibly responds to the pH change.

Purified pristine Tube@Rice SWNTs suspended in toluene were purchased from Rice University. Raw HiPco SWNTs were purchased from Carbon Nanotechnologies, Inc., and were purified by the method described in ref 11. Because similar results were obtained with these two types of SWNTs, we reported the results here only for Tube@Rice SWNTs for the sake of clarity.

The facile routine for preparation of water-soluble SWNTs was a modification of the acid oxidative method developed in Smalley's group.[7] In a typical experiment, 14 mg of SWNTs were added into 5 mL of a 9:1 concentrated H_2SO_4/30% H_2O_2 aqueous solution. The mixture was stirred for 30 min. After the reaction, 15 mL of the 9:1 concentrated H_2SO_4/30% H_2O_2 solution was added into the mixture. Then the mixture was divided into six aliquots in test tubes. Each aliquot was placed in an ultrasonic bath (Branson model 1510) and was sonicated for a different period of time, ranging from 0 to 5.0 min. Each resulting SWNT dispersion was diluted using 250 mL of distilled water and then was filtered through a 0.4 μm Millipore polycarbonate filter membrane. The resulting six SWNT mats were continuously washed using 10 mM NaOH solution and distilled water until the pH of the filtrates was 7. Then the wet SWNT mats were separated from the filters by dispersing them in distilled water. Six aqueous solutions of the SWNTs (0.03 mg/mL) were prepared by sonication for 1−2 min. No tube precipitation was observed from these solutions after a month (the right vial in Figure 1). A similar result was observed for a 0.15 mg/mL solution. As-treated SWNTs were also soluble in 2-propanol.

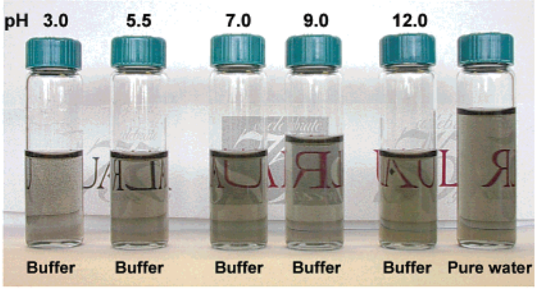

Figure 1. As-treated SWNTs (5-min sonication) in different pH buffer solutions.

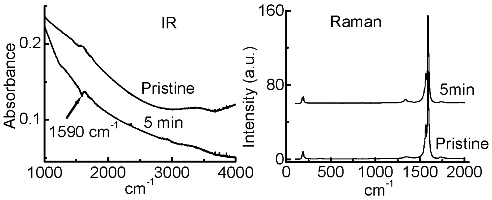

Figure 2. IR and Raman (532-nm excitation) spectra of thin films of pristine SWNTs and as-treated SWNTs (5-min sonication).

IR spectra of the acid-sonicated samples show that the intensity of the 1590-cm^{-1} band of the carboxylate COO^- groups[5b,8] increases (Figure 2), suggesting that carboxylate groups are introduced on the SWNTs. X-ray photoelectron spectroscopy (XPS) analysis on the composition of the as-treated SWNT mats under different sonication times indicates that the oxygen content is fairly constant between 9 and 14 atom % regardless of the sonication (Figure 1S, Supporting Information). Raman spectra show that there is no significant difference between the samples before and after oxidation, suggesting that the tubular structure of SWNTs is undisrupted (Figure 2). The carboxylate groups may be formed mainly on the sites of the defects and the ends of the tubes. This conclusion is further supported by the absorption spectra where the van Hove features of SWNTs are retained as shown below.

The pH dependence of the water-soluble SWNTs is reported here for the sample sonicated for 5 min,[12] although similar results were observed for the other samples. Figure 1 shows the sample dispersed in different pH buffers which were prepared according to ref 13. The buffers have an ionic strength of ~0.01 M. The sample is soluble in the buffers with pH > 3. [14] The solutions are stable over 12 h which is long enough for optical measurements. For pH ≤ 3, the sample solution is not stable, and aggregation occurs within minutes.[14]

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10.1021/ja027861n CCC: $22.00

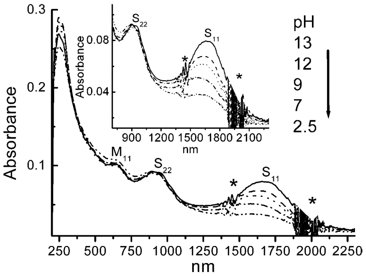

Figure 3. Absorption spectra of as-treated SWNTs (5-min sonication) in different pH buffers. The asterisks indicate the noise caused by the subtraction of the corresponding aqueous buffer background.

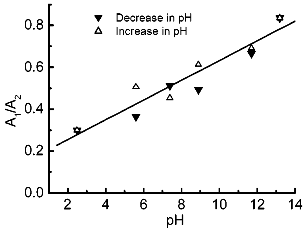

Figure 4. Normalized absorbance of the S_{11} band, plotted as the ratio A_1/A_2 of the peaks S_{11} and S_{22} of an as-treated SWNT sample (5-min sonication), reversibly responds to the pH change.[15]

Figure 3 shows the absorption spectra of the SWNT sample in different pH buffer solutions. The peaks S_{11} and S_{22} are assigned to the first and second interband transitions in the density of states (DOS) of semiconducting SWNTs,[5a,11] respectively. The intensity of the peak S_{11} decreases with the decrease of pH, while the peak S_{22} remains unchanged. The first interband transition peak M_{11} of metallic SWNTs is also not sensitive to the pH change. This result indicates that the change in the concentration of H^+ and OH^- causes an electronic structure change in semiconducting SWNTs by refilling or depleting their valence band.[5a] Previous experiments have shown that the intensity of the S_{11} band increases after annealing at high temperatures, which is related to the desorption of residual acids introduced during purification. Our results further indicate that the S_{11} band of as-treated SWNTs can respond to the pH change in an aqueous solution.

More significantly, the intensity of the first transition S_{11} of semiconducting SWNTs is reversibly tunable by changing pH as shown in Figure 4 where A_1/A_2 is the absorbance ratio of the peak S_{11} and the peak S_{22}. To our knowledge, this is the first reported observation that the optical properties of SWNTs can be reversibly tuned by pH in aqueous solutions.

The intensity change in the S_{11} band versus pH could be caused by mechanisms such as intercalation and deintercalation of H^+ ions in the SWNT bundles,[5a,11] diffusion of H^+ inside the tubes through the open sites at the defects and the ends of the tubes,[16] and the surface modification with the carboxylate groups which may serve as pH-sensing groups through protonation and deprotonation.[6] It appears that the intercalation mechanism is not the major mechanism in this work because the pristine SWNTs are not sensitive to pH when dispersed in the pH buffers containing 0.5 wt % Triton X-100 surfactant which is a solubilizing agent for the pristine SWNTs in water. In the control experiment with the pH buffers containing the surfactant, as-treated SWNTs retain the response to pH (Figure 2S, Supporting Information). This result indicates that the observed pH dependence of the S_{11} band of as-treated SWNTs is uniquely related to the surface modification with carboxylate groups and is unaffected by the surfactant. The protonation and deprotonation of the carboxylate groups could cause electrostatic doping/charging to the nanotube and therefore shift the Fermi level.[17] Further study is needed to elucidate the mechanism for better surface modification and control.

Our results suggest that surface modification of SWNTs is a promising way for making chemically selective SWNT interfaces, which may open new exciting opportunities for applications.

Acknowledgment. We thank one reviewer for bringing refs 5c and 10b to our attention. Financial support from ARO under Award No. DAAD 190210140 and ONR is greatly appreciated.

Supporting Information Available: Figure 1S, XPS determined atom % C and O of as-treated SWNTs plotted as a function of sonication time; Figure 2S, absorption spectra of pristine and as-treated SWNTs in pH buffer solutions with 0.5% Triton X-100 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) For the sample, the average diameter is 1.3 nm, and the length is in the range from several hundred nanometers to a few micrometers.
(13) *CRC Handbook of Chemistry and Physics*, 82nd ed.; Lide, D. R., Ed.-in-Chief; CRC Press: New York, 2001−2002; p8−43.
(14) Due to deprotonation at pH > 3.0, the carboxylic groups acquire charges which result in mutual repulsion between the tubes, hydration shells around the tubes, and a consequent solubility of the tubes.[7b] At pH ≤ 3.0, the SWNTs are protonated, and aggregation occurs due to van der Waals forces.
(15) The measurements were done by dissolving the sample in a pH buffer, measuring the absorption spectrum, then recollecting the sample by filtration, and dissolving it again in the next pH buffer for measurements.
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JA027861N